ELECTROCHEMICAL AND HYDROGEN SORPTION PROPERTIES OF AB_5–TYPE ALLOYS WHERE A – La, Ce; B – Ni, Co, Mn, Fe, Cu, Cr, Al

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Abstract. Like other accumulator types Ni-MH batteries are unable to keep high characteristics in the temperature range -30°C to +40°C. To solve this problem the negative electrode material – intermetallic compound (IMC) hydride – must have dissociation pressure of 0.1–1.5 atm in this temperature interval. The IMC composition was calculated with mathematic model. The model describes dependence of IMC hydrides properties on IMC composition. Using calculation results series of alloys were prepared and their hydrogen absorption and electrochemical properties were studied. The best alloy is $CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$. The sample has discharge capacity 275 mAh/g, keeps 95% of this value at 40°C and 40% at -30°C.

Keywords: Ni-MH batteries, intermetallic compounds, IMC hydrides, mathematical model

1. Introduction

Today nickel metal hydride batteries (Ni-MH) are one of most power-capacious and reliable accumulators [1–6]. The discharge capacity of modern Ni-MH batteries is equal and in some cases greater than that of disposable non-rechargeable alkaline batteries. Like other accumulators, Ni-MH batteries can't preserve high capacity characteristics at temperatures from –30 to +40°C. Working temperature interval of accumulator depends on properties of negative MH-electrode. MH-electrode properties are determined by hydrogen sorption properties of intermetallic compound (IMC). The dissociation hydrogen pressure of alloy or IMC should be in the interval of 0.1–1.5 atm for its application in MH- electrode. Experimental search of alloy compositions satisfying these pressure conditions is very difficult. In our work we used mathematical model where hydride properties are function of compositions of alloy components. For this purpose the large database of properties for alloys of AB_5-type, where A: La, Ce, Mm, Gd, Nd, and B: Ni, Co, Al, Cu, Fe, Mn, Cr was analyzed. In a result of calculation the series of alloys were prepared. Their electrochemical and hydrogen sorption properties were measured at –30 to +40°C.

2. Alloys composition calculation

In this paper an attempt of IMC electrochemical properties prognosis was made by the calculation of thermodynamic parameters of their hydrides.

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TABLE 1. Thermodynamic characteristics of the AB_5 IMC hydrides chosen for the data base

IMC	ΔH, kJ/mol H_2	ΔS, J/K mol H_2	Source
$Ce_{0.7}Nd_{0.3}Ni_{2.5}Cu_2$	15.7	72.2	[8]
$LaNi_{4.9}Cu_{0.1}$	28.5	97.4	[9]
$LaNi_{4.5}Cu_{0.25}Al_{0.25}$	39.0	115.0	[10]
$LaNi_4Cu$	48. 5	115.5	[9, 11]
$LaNi_3Cu_2$	31.0	96.0	[12]
$LaNi_2Cu_3$	34.8	109.0	[12]
$CeNi_{2.5}Cu_{2.5}$	24.1	97.1	[13]
$CeNi_{4.25}Cu_{0.75}$	25.2	86.6	[14]
$La_{0.3}Ce_{0.7}Ni_5$	25.3	109.0	[15]
$La_{0.2}Ce_{0.8}Ni_{4.7}Cu_{0,3}$	24.8	108.4	[14]
$La_{0.2}Ce_{0.8}Ni_5$	23.8	108.8	[14]
$CeNi_{2.5}Co_{2.5}$	20.7	81.1	[15]
$CeCo_5$	49.5	32.6	[15]
$CeNi_{2.5}Cu_{2.3}Al_{0.2}$	15.3	53.7	[8]
$CeCu_2Ni_{2.5}Al_{0.5}$	28.6	70.2	[8]
$CeNi_{4.4}Al_{0.6}$	18.9	77.7	[16]
$CeNi_{4.5}Al_{0.5}$	18.0	78.4	[16]
$CeNi_5$	22.2	111.0	[15, 14]
$CeNi_4Co$	30.5	133.0	[15]
$La_{0.1}Ce_{0.9}Ni_{4.95}Al_{0.05}$	27.6	97.9	[17]
$LaCo_5$	45.1	110.0	[15]
$LaNi_2Co_3$	43.9	128.0	[18]
$LaCo_2Ni_3$	31.0	16.0	[19]
$LaCu_{1.5}Ni_{3.5}$	35.3	116.6	[11]
$LaNi_4Al$	49.2	118.8	[19]
$LaNi_{4.6}Mn_{0.4}$	25.6	75.0	[9]
$LaCoNi_4$	32.0	112.0	[18]
$LaNi_{4.9}Al_{0.1}$	32.6	115.7	[8, 20]
$LaNi_2Al_{0.25}$	33.7	110.9	[21]
$LaNi_5$	30.9	107.7	[22, 23]
$NdNi_{4.5}Al_{0.5}$	47.0	154.9	[24]
$NdNi_4Al$	54.1	174.7	[24]
$NdNi_{3.5}Al_{1.5}$	54.3	173.6	[24]
$LaNi_{2.5}Fe_{2.5}$	37.2	97.5	[25]
$LaNi_4Fe$	34.5	92.7	[25, 9]

The mathematical model was used for calculation of ΔH and ΔS of hydrogen desorption reaction, because direct calculation hydride formation heat is very difficult task with inaccurate result.

And so we have used empirical and semiempirical model. The thermodynamic parameters change monotonously in the single phase region of solid solution according to the Wegard law. Therefore a large experimental thermodynamic data massive can be

approximated with function of its composition. Such model was developed in our laboratory for calculation thermodynamic characteristics multicomponent stoichiometric alloys [7]. The lattice constants, ΔH and ΔS values of hydrogen desorption reaction can be described by polynomial:

$$F(x)=Y_0+\sum A_i \cdot x_i + \sum B_{ij} \cdot x_i \cdot x_j \qquad (j \geq i),$$

where x are IMC components concentration; Y_0, A, B are constants.

Experimental data of the parameters are used for determining the following coefficients of the polynomial (A_i,B_{ij}…). For the solving equation system the minimal number of initial data in data base is:

$$N=2i+(i^2-i)/2,$$

where i are independent metal concentrations.

The alloys constituting the data base in resent task are present in Table 1. The calculation conditions are: dissociation pressure 0.09–0.2 atm at –30°C and 1–3 atm at 40^0C. It was obtained near 250 results of calculations of the IMC compositions. Only three was chosen for the experimental study:

$CeMn_{0.25}Co_{0.75}Al_{0.5}Ni_{3.5}$
$CeMn_{0.5}Co_{0.5}Fe_{0.25}Al_{0.4}Ni_{3.35}$
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$.

3. Experimental

Alloys were prepared by arc-melting the mixtures of pure initial metals under argon atmosphere. With the purpose of homogenization, the alloys were remelted four times. The structure and phase composition of alloys was examined by powder X-ray diffraction. The refinement of diffraction profiles was performed using the Rietveld method.

The hydrogen absorption properties were studied by measuring PCT isotherms using a Siewerts type apparatus at a hydrogen pressure below 100 atm. The thermodynamic characteristics (ΔH and ΔS) of IMC hydrides were calculated from Vant-Hoff equation by using desorption isotherms data at temperatures from –30°C to 40°C.

The electrochemical experiments were carried out in a three-electrode electrochemical glass cell with Hg/HgO electrode as the reference. The electrolyte was 6 M KOH solution. The MH electrodes were prepared by cold-pressing of mixture of IMC powder (20%) with copper powder (80%) in a pellet. Samples were charged with current density of 200 mA/g during 2–3 h. The resting time before discharging was 10 min. All samples underwent 2–3 charge-discharge cycles for the activation. The discharge capacity was checked at current densities of 100, 200 and 400 mA/g. Discharge curves were measured at temperatures 40°C, 23°C, 0°C and -30°C. Discharge curves at temperatures of 40^0C, 0^0C and -30^0C have only qualitative character because only working part of the cell was thermostated and the reference electrode was at room temperature. High rate discharge ability of alloys was calculated by following equation:

$$C_R = \frac{C_{400}}{C_{400} + C^*_{50}} \times 100\,\%\,,$$

where C^*_{50} is resting MH- electrode capacity that was measured after discharging of 400 mA/g with discharge current density of 50 mA/g.

The cycle life of electrode wasn't investigated but it was stated that after 15 charge-discharge cycles no loss in discharge capacity was noticed.

4. Results and discussion

X-ray diffraction analysis indicates that the main phase in all samples was $CaCu_5$-type phase. The cell parameters of IMC are presents in Table 2.

Hydrogen desorption isotherms of the samples are present in the Fig. 1. Hydrogen sorption properties of IMC hydrides are summarized in Table 3.

TABLE 2. Cell parameters of $CaCu_5$- type structure alloys

IMC	a (Å)	c (Å)	V (Å^3)
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.5}$	4.9394 ± 0.0004	4.0732 ± 0.0004	86.062 ± 0.013
$CeMn_{0.5}Co_{0.5}Fe_{0.25}Al_{0.4}Ni_{3.35}$	4.9481 ± 0.0006	4.0757 ± 0.0006	86.419 ± 0.020
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$	4.9428 ± 0.0007	4.0727 ± 0.0007	86.171 ± 0.023

TABLE 3. Hydrogen sorption properties of IMC hydrides

IMC	ΔH_{des} (kJ/mol H_2)	ΔS_{des} (J/K mol H_2)	t (^{o}C)	P_{dis} (atm)	H_2 content	
					mass %	H/IMC
$CeMn_{0.25}Co_{0.75}Al_{0.5}Ni_{3.5}$	28 ± 2	103 ± 6	40	4.84	1.1(0)	4.6
			25	2.25	1.1(3)	4.8
			0	1.03	1.1(9)	5.0
			-30	0.19	1.2(7)	5.3
$CeMn_{0.5}Co_{0.5}Fe_{0.25}Al_{0.4}Ni_{3.35}$	30 ± 1	99 ± 4	40	1.49	1.2(5)	5.3
			25	0.7	1.2(6)	5.3
			0	0.25	1.3(0)	5.4
			-30	0.05	1.3(3)	5.6
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$	30 ± 2	97 ± 7	40	1.12	1.2(9)	5.4
			25	0.48	1.3(1)	5.5
			0	0.20	1.3(5)	5.6
			-30	0.04	1.3(8)	5.8

Analysing the obtained data we can see that increase of cobalt content by partial substitution of manganese and nickel leads to decreasing hydrogen capacity, increasing hydrogen dissociation pressure and decreasing hydrogen dissociation enthalpy; iron addition leads to same result but the change in the properties is less significant.

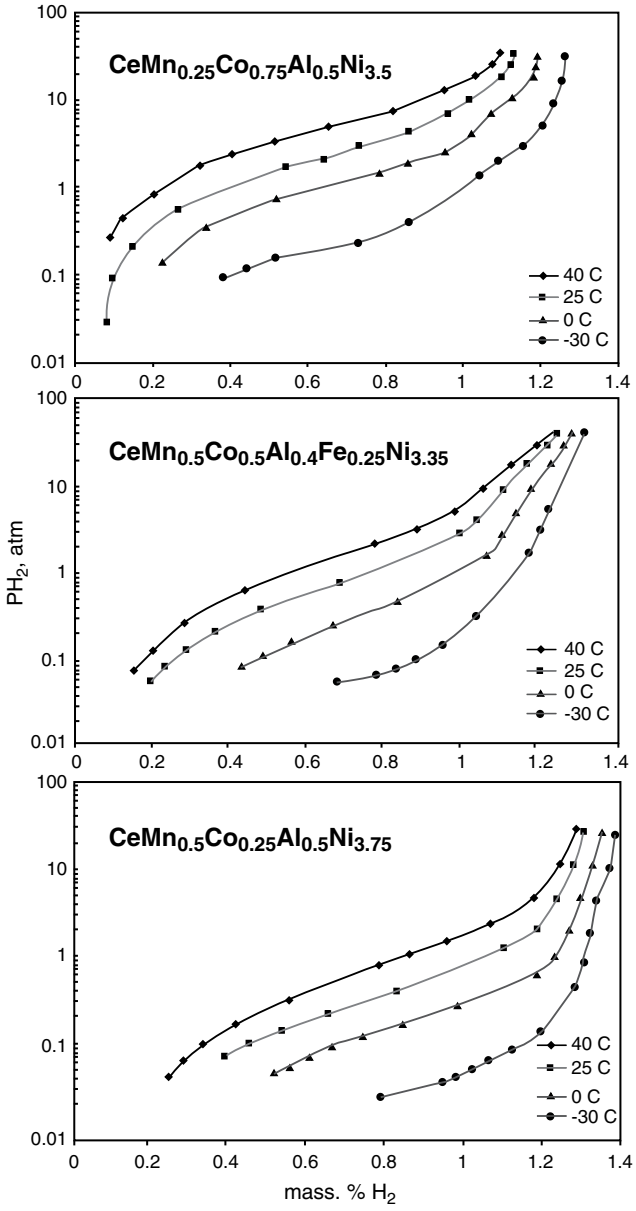

Figure 1. PCT isotherms of studied IMC hydrides

The hydrogen sorption properties of AB_5 alloys determined during experiment were slightly different from calculated values (Table 4). This divergence can be explained by two ways.

TABLE 4. The comparison of hydrogen desorption enthalpies (kJ/mol H_2) and hydrogen dissociation pressures of IMC hydrides (atm) at temperatures 40^0C and -30^0C that were obtained by the calculation (ΔH^C, $P_{40}{}^C$, $P_{-30}{}^C$) and by the experiment (ΔH^E, $P_{40}{}^E$, $P_{-30}{}^E$)

IMC	ΔH^C	ΔH^E	$P_{40}{}^C$	$P_{40}{}^E$	$P_{-30}{}^C$	$P_{-30}{}^E$
$CeMn_{0.25}Co_{0.75}Al_{0.5}Ni_{3.5}$	23	28	1.55	4.84	0.12	0.19
$CeMn_{0.5}Co_{0.5}Fe_{0.25}Al_{0.4}Ni_{3.35}$	24	30	1.2	1.49	0.13	0.05
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$	24	30	2.6	1.12	0.1	0.04

At first it is imperfection of mathematic modeling. Using more initial data will increase the prognosis accuracy. And besides we understand that initial data were obtained in different laboratories with different accuracy. Secondly the divergence can happens due to the loss of Mn and Ce during the alloy melting.

However we suppose that hydrogen sorption properties of these IMC satisfied the MH-electrode requirements.

Maximum discharge capacity of samples 250–280 mAh/g is realized at room temperature at discharge current density 100 mA/g. Discharge curves of MH-electrodes at discharge current density 100 mA/g and different temperatures are present in Fig. 2, electrochemical properties of IMC are summarised in Table 5.

TABLE 5. Electrochemical properties of MH-electrodes with studied IMC

IMC	t (^{o}C)	Discharge capacity		C_R (%)
		C_{100} (mAh/g)	C_{400} (mAh/g)	
$CeMn_{0.25}Co_{0.75}Al_{0.5}Ni_{3.5}$	40	227	225	97.0
	25	239	192	79.3
	0	211	117	52.0
	-30	88	31	33.7
$CeMn_{0.5}Co_{0.5}Fe_{0.25}Al_{0.4}Ni_{3.35}$	40	170	78	43.1
	25	218	86	39.6
	0	150	60	39.1
	-30	68	28	38.4
$CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$	40	261	254	97.0
	25	275	241	86.1
	0	247	189	75.6
	-30	112	45	40.2

The dependence of discharge capacity at discharge current density of 100 mA/g on temperature is present in Fig. 3.

Analyzing electrochemical properties of samples we can make following conclusions:

– Discharge capacity of MH-electrode increase with nickel content in IMC
– Partial substitution of nickel and aluminum by iron leads to significant decrease of discharge characteristics

– Partial substitution of nickel and manganese by cobalt result in insignificant changes of the discharge ability but leads to its small decrease at low temperatures

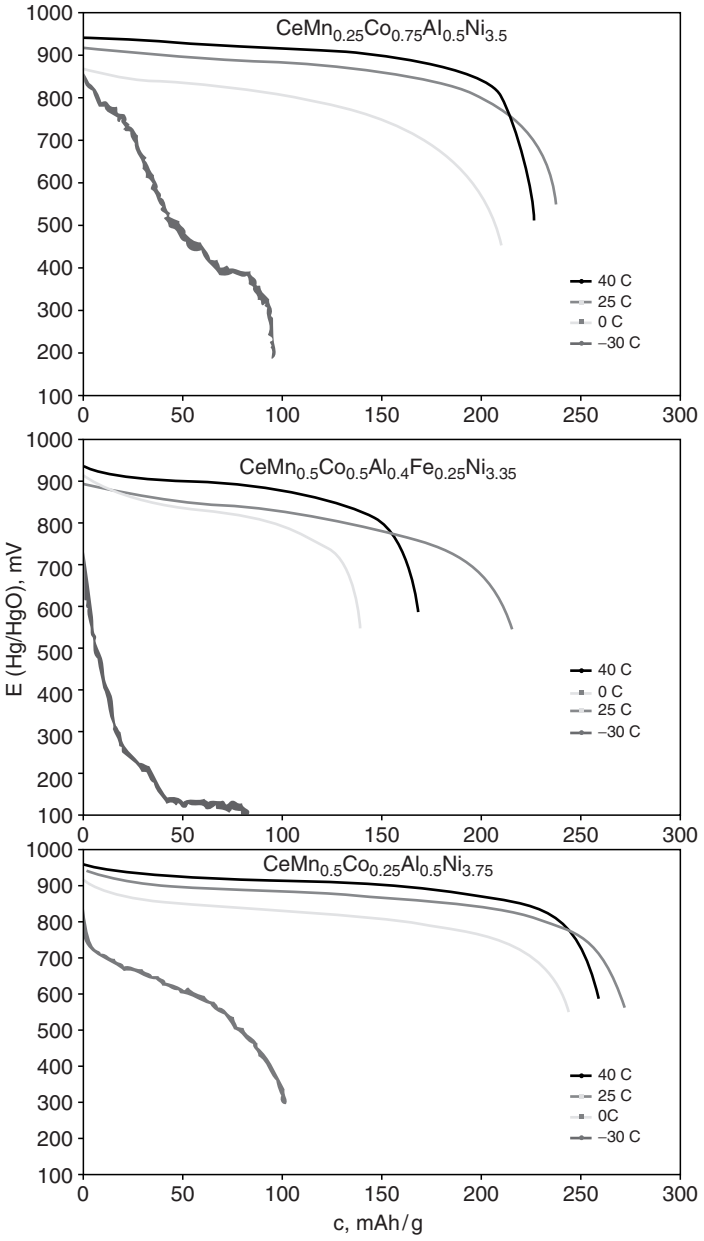

Figure 2. Discharge curves of MH-electrodes at discharge current density 100 mA/g

IMC $CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$ shows best electrochemical properties among studied alloy series. Its hydrogen capacities at all temperatures are maximal among these alloys. And besides nickel concentration is highest in this series that yields a best electrocatalytic activity. Discharge capacity $CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$ (275 mAh/g at 100 mA/g and room temperature) is comparable with commercial MH-electrode alloys (250–310 mAh/g). Discharge capacity $CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$ depends on temperature nearly three times weaker than capacity of the commercial alloys [2].

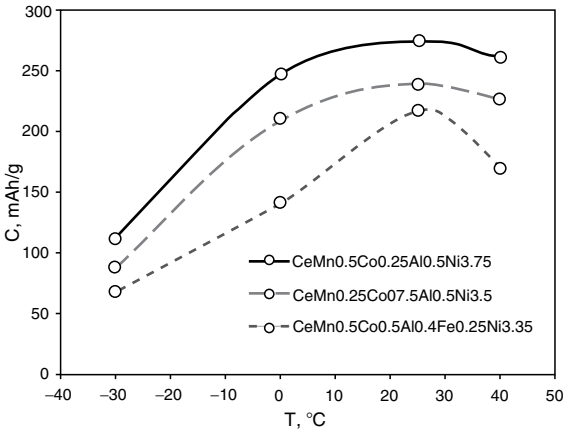

Figure 3. The dependence discharge capacity $C_{100\ mA/g}$ on temperature

5. Conclusions

The principal possibility of mathematic calculation the composition of IMC with required hydrogen properties is shown in this paper. Although the divergence between calculated and experimental hydrogen sorption characteristics all samples satisfied the working conditions of MH-electrodes. Hydrogen content in IMC hydrides is in the range of 1.1–1.3 mass%, discharge capacities at 100 mA/g and room temperatures are 218–275 mAh/g. The best sample $CeMn_{0.5}Co_{0.25}Al_{0.5}Ni_{3.75}$ has discharge capacity 275 mAh/g, keeps 95% of this value at 40°C and 40% at -30°C.

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